OIPE JC90
JUL 2 6 2004
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D E C L A R A T I O N

In the matter of U. S. Patent Application Ser. No. 10/803,456 in the name of Masataka KANO

I, Makoto ASANO, of Kyowa Patent and Law Office, 2-3, Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare and say:

that I am thoroughly conversant with both the Japanese and English languages; and

that the attached document represents a true English translation of United States Patent Application Serial No. 10/803,456 dated March 18, 2004.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief and believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: July 16, 2004

Makoto Asano

Makoto ASANO

ORGANIC BISTABLE ELEMENT, ORGANIC BISTABLE MEMORY DEVICE USING THE SAME, AND METHOD FOR DRIVING SAID ORGANIC BISTABLE ELEMENT AND ORGANIC BISTABLE MEMORY DEVICE

[BACKGROUND OF THE INVENTION]

Field of the Invention

The present invention relates to an organic bistable element, which can be operated at a low drive voltage and in which the degree of a difference in threshold voltage between information writing and information reading can be regulated by regulating the thickness of members constituting the element, a memory device using the same, and a method for driving the organic bistable element and the memory device.

Background Art

A conventional organic bistable element has a laminate structure in which a ferroelectric layer is interposed between a pair of electrodes. For example, anthracene and TTF-CA (an alternately laminated charge transfer complex of tetrathiafulvalene and tetrachloro-p-benzoquinone) have been studied for use as compounds for constituting the ferroelectric layer (see, for example, Japanese Patent Laid-Open No. 345431/2001 on pages 2 and 3, Fig. 1).

Further, an organic bistable element has also been proposed in which a laminate having a three-layer structure comprising an electrically conductive thin film interposed between two layers of low-electrically conductive organic thin film having a two-layer structure is used instead of the ferroelectric layer and is interposed between a pair of electrodes. In this case, AIDCN (2-amino-4,5-dicyanoimidazole) is used as the material for constituting the low-electrically conductive organic thin film (see, for example, pamphlet of WO 02/37500 on pages 6 to 8, Fig. 2).

The organic bistable element disclosed in Japanese Patent Laid-Open No. 345431/2001 suffers from a problem that, due to a relatively high switching voltage, power consumption in

driving is increased. On the other hand, the organic bistable element disclosed in the pamphlet of WO 02/37500 is advantageous in that, as compared with the construction in which only the ferroelectric layer is interposed between the electrodes, the switching voltage can be reduced. Since, however, the drive voltage of the element depends upon compounds constituting the organic thin films, a power source should be newly provided for each compound, or the output voltage should be regulated using a variable power source.

Further, in an actual organic bistable element, providing a suitable level of difference in threshold voltage between information writing and information reading is preferred. In the prior art technique, however, the difference level of threshold voltage between information writing and information reading could not have been regulated.

[SUMMARY OF THE INVENTION]

The present inventor has now found that, when a laminate, to be provided between electrodes, is constituted by a plurality of organic thin films with regulated thicknesses or formed of respective different materials, an organic bistable element using this laminate can be driven at a low voltage and, at the same time, the degree of a difference in threshold voltage between information writing and information erasing is variable. The present invention has been made based on such finding.

Accordingly, an object of the present invention is to provide an organic bistable element, which can be driven at a low voltage and in which the degree of a difference in threshold voltage between information writing and information erasing is variable, an organic bistable memory device using the same, and a method for driving the organic bistable element and the memory device.

According to one aspect of the present invention, there is provided an organic bistable element having a laminate structure comprising a laminate interposed between a first

electrode and a second electrode, said laminate comprising two or more layers of organic thin film which are each dielectric and are different from each other in electrical conductivity, said two or more layers of organic thin film having been stacked on top of each other through an electrically conductive thin film.

According to another aspect of the present invention, there is provided an organic bistable memory device comprising: a first electrode and a second electrode provided orthogonally to each other; and a laminate provided in an area, between the first electrode and the second electrode, which is an intersecting area of the first electrode and the second electrode, said laminate comprising two or more layers of organic thin film, which are each dielectric and are different from each other in electrical conductivity, said two or more layers of organic thin film having been stacked on top of each other through an electrically conductive thin film.

According to a further aspect of the present invention, there is provided a method for driving the organic bistable element, said method comprising the step of limiting, in writing information into the organic bistable element, current, which flows in either a positive bias side or a negative bias side, to prevent a predetermined level or more of current from flowing in the organic bistable element.

The organic bistable element of the present invention can be driven at a low voltage, and the degree of a difference in threshold voltage between information writing and information erasing is variable. Further, an organic bistable memory device, which is less likely to cause malfunction, can be realized by limiting current, which flows in either a positive bias side or a negative bias side, to prevent a predetermined level or more of current from flowing in the organic bistable memory device.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 is a schematic cross-sectional view showing one embodiment of a basic laminate structure of the organic bistable element according to the present invention;

Fig. 2 is a typical diagram of an organic bistable memory device in which organic bistable elements according to the present invention are disposed in a simple matrix form;

Fig. 3 is a plan view showing a memory cell array of the organic bistable memory device shown in Fig. 2;

Fig. 4 is a cross-sectional view taken on line A-A' of the memory cell array shown in Fig. 3;

Fig. 5 is a typical cross-sectional view of an organic bistable memory device comprising the organic bistable element according to the present invention in combination with a thin-film transistor;

Fig. 6 is a graph showing characteristics obtained by applying a negative voltage to the organic bistable element according to the present invention;

Fig. 7 is a graph showing characteristics obtained by applying a positive voltage to the organic bistable element according to the present invention;

Fig. 8 is a graph showing the relationship between layer thickness difference of organic thin films and threshold voltage difference in organic bistable elements;

Fig. 9 is a graph showing current/voltage characteristics in the case where an organic bistable element is driven using a limiter; and

Fig. 10 is a graph showing current/voltage characteristics in the case where an organic bistable element is driven without a limiter.

[DETAILED DESCRIPTION OF THE INVENTION]

The organic bistable element according to the present invention, the memory device using the element, and the method for driving them will be described with reference to the accompanying drawings.

Fig. 1 is a diagram illustrating a basic laminate structure of the organic bistable element according to the present invention. An organic bistable element 1 according to the present invention has a laminate structure in which a first

electrode 3, a laminate 4, and a second electrode 5 are stacked in that order on a substrate 2. The laminate 4 comprises an organic thin film 4a (hereinafter referred to also as "organic thin film A"), an electrically conductive thin film 4c, an organic thin film 4b (hereinafter referred to also as "organic thin film B") stacked in that order.

The substrate 2 is used for stacking thereon a first electrode 3, an organic thin film A, an electrically conductive thin film 4c, an organic thin film B, and a second electrode 5 in that order. The substrate 2 is formed of an inorganic base material such as glass, silicon, or quartz or the following organic base material. The substrate 2 is used for supporting the layers provided thereon and may be omitted. When the substrate 2 is used, however, the handleability of the organic bistable element is improved because rigidity can be imparted to the organic bistable element. Further, the provision of the substrate facilitates the arrangement of a large number of the elements on the substrate to form a memory device or the like.

Organic base materials usable herein include polyamides, polyacetals, polybutylene terephthalate, polyethylene terephthalate, polyethylene naphthalate, syndiotactic polystyrene, polyphenylene sulfide, polyetherether ketone, liquid crystal polymers, fluororesins, polyether nitrile, polycarbonate, modified polyphenylene ether, polycyclohexene, polynorbornene resins, polysulfone, polyether sulfone, polyarylate, polyamideimide, polyetherimide, and thermoplastic polyimides. The organic base material, however, is not limited to these materials, and conventional plastics may also be used. In particular, when the substrate 2 is formed of an organic base material, the use of a thin flexible film having a thickness of about 5 to 300 μm can provide a flexible organic bistable element.

The first electrode 3 is preferably formed of, for example, a metallic thin film, a relatively high electrically conductive organic thin film, or a thin film of electrically conductive perovskite oxide from the viewpoint of providing proper bonding

to the organic thin film 4 as a bistable layer. The metallic thin film may be formed of, for example, a highly electrically conductive metal such as Al (aluminum), Pt (platinum), Au (gold), Ag (silver), Fe (iron), Ni (nickel), Cr (chromium), Cu (copper), Ti (titanium), Hf (hafnium), Zn (zinc), Zr (zirconium), Mo (molybdenum), or Ta (tantalum). The highly electrically conductive organic thin film may be formed of PEDOT (3,4-polyethylenedioxythiophenylene/polystyrene sulfate), or properly doped polyaniline, polyacetylene, fullerene, carbon nanotube or carbon nanowire. The electrode may also be formed of a thin film of electrically conductive perovskite oxide. Suitable electrically conductive perovskite oxides include IrOx, MnOx, NiOx, CuOx, or RuOx or properly doped product of the above oxides. The thickness of the first electrode 3 is preferably about 0.5 nm to 5 μm although the thickness varies depending upon the electrical conductivity of the material.

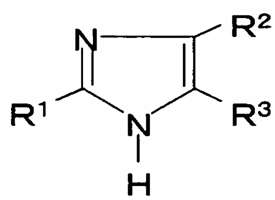
In the organic bistable element 1 according to the present invention, a laminate 4 comprising an organic thin film 4a, an electrically conductive thin film 4c, and an organic thin film 4b stacked in that order as viewed from the first electrode 3 side is interposed between the first electrode 3 and the second electrode 5. The organic thin film 4a and the organic thin film 4b are each dielectric and are different from each other in electrical conductivity. Specific examples of methods usable for varying the electrical conductivity include (i) a method in which one of dissimilar materials different from each other in electrical conductivity is used in one of the organic thin film 4a and the organic thin film 4b and the other material is used in the other film and (ii) a method in which the organic thin film 4a and the organic thin film 4b are formed using an identical material in such a manner that the thickness of the organic thin film 4a is different from that of the organic thin film 4b.

An organic material or a combination of two or more organic materials selected from 2,4,5-substituted imidazole, tris-8-hydroxyquinoline aluminum (AlQ), 7,7,8,8-tetracyanoquinodimethane (TCNQ), N-3-nitrobenzylidene-p-

phenylenediamine (NBPDA), NBPDA derivatives, anthracene and the like is suitable for the formation of the organic thin film 4a or 4b.

In the method (i), the electrical conductivity of the organic thin film 4a and the electrical conductivity of the organic thin film 4b can be made different from each other by properly selecting organic compounds for constituting the organic thin film 4a and the organic thin film 4b. In this case, the thickness of the organic thin film 4a may be the same as the thickness of the organic thin film 4b. Alternatively, the degree of a difference in electrical conductivity may be regulated by providing a proper level of difference in thickness between the organic thin film 4a and the organic thin film 4b from the viewpoint of regulating the electrical conductivity.

In the method (ii), the organic thin film is preferably formed of an organic compound having at least one electron-donating group and at least one electron-receiving group represented by formula (I):



(I)

wherein, in R^1, R^2, and R^3,

one or two of them each independently represent an electron-donating group selected from the group consisting of -H, $-NH_2$, -NHR, $-NR_2$, -SR, -X, $-CX_3$, -OH, $-OCH_3$, -OR and -R, wherein R represents a straight chain or branched chain alkyl group having 1 to 24 carbon atoms in which one or at least two methylene groups in the alkyl group are optionally substituted by a substituent of -O-, -S-, -CO-, -CHW-, wherein W represents -F, -Cl, -Br, -I, -CN or $-CF_3$, -CH=CH-, or -C≡C-, provided that a plurality of said substituents are not adjacent to each other, and X represents -F, -Cl, -Br, or -I; and

the remaining group or groups of R^1, R^2, and R^3 each independently represent an electron-receiving group selected

from the group consisting of -CN, -NO_2, -COR, -COOH, -COOR, and -SO_3H.

In the method (ii), preferably, the above compound is used as the organic compound, and one of the organic thin films, i.e., a first organic thin film, has a thickness of 10 nm to 200 nm while the thickness of the other organic thin film is 1.1 to 10 times larger than the thickness of the first organic thin film. When the thicknesses of the organic thin films are in the above-defined respective thickness ranges, the difference in electrical conductivity of both the thin films is such that the electrical conductivity of one of the thin films, i.e., the thin film having larger electrical conductivity, is approximately 10% to 100% larger than the electrical conductivity of the other thin film having smaller electrical conductivity.

The organic thin films 4a and 4b may be formed by a gas phase method such as a vacuum deposition method using the above organic compound, or by a coating method such as spin coating using a solution prepared by dissolving an organic compound in a suitable solvent. The thickness of the organic thin film 4 is suitably 5 to 1000 nm, particularly preferably 10 to 200 nm.

As with the first electrode 3, the second electrode 5 is formed of a metallic thin film, a relatively high electrically conductive organic thin film, a thin film of an electrically conductive perovskite oxide or the like. The thickness of the second electrode 5 may be the same as that of the first electrode 3.

The organic bistable element according to the present invention is suitable for use in a memory device. When the organic bistable element is used as a memory, whether the organic bistable element 1 is in ON state or in OFF state can be judged by applying a positive or negative pulse voltage to the organic bistable element for a very short period of time to bring the state to writing (ON state) or erasing (OFF state) and then applying a constant voltage, which is a voltage smaller than the absolute value of the pulse voltage for writing or erasing, for a

very short period of time. The characteristics of the element can be examined by applying a positive or negative voltage across the first electrode 3 and the second electrode 5 to measure current which flows across both the electrodes, or allowing a positive or negative current to flow across both the electrodes to measure voltage across both the electrodes.

In the present invention, in writing information in the organic bistable element, current, which flows in either a positive bias side or a negative bias side, is limited to prevent a predetermined level or more of current from flowing in the organic bistable element. Preventing a given level or more of current from flowing in the organic bistable element ensures reliable ON/OFF switching and thus can realize a memory device which is less likely to cause malfunction. The current on the positive bias side or negative bias side can be limited by regulating the current with a measuring device or by using a constant-current diode to prevent a predetermined value or more of current from flowing in the organic bistable element.

The organic bistable element according to the present invention can be used to prepare an organic bistable memory device as shown in Fig. 2 (a typical view). Fig. 3 is a partially enlarged plan view of a memory cell array of an organic bistable element shown in Fig. 2, and Fig. 4 is a cross-sectional view taken on line A-A′ of Fig. 3.

As shown in Fig. 2, the organic bistable memory device 7 includes a memory cell array 8 comprising organic bistable elements 1 arranged in a simple matrix form, an electrode for selective information writing in the organic bistable element 1 or selective information reading from the organic bistable element 1, and various circuits which include, for example, a first electrode 3, a first drive circuit 9 for selectively controlling the first electrode 3, a second electrode 5, a second drive circuit 10 for selectively controlling the second electrode 5, and a signal detection circuit (not shown).

The memory cell array 8 includes first electrodes (word lines) 3 for line selection and second electrodes (bit lines) 5 for

row selection arranged orthogonally to the first electrodes 3. Specifically, the first electrodes 3 are arranged at a predetermined pitch in direction X, and the second electrodes 5 are arranged at a predetermined pitch in direction Y orthogonal to direction X. The signal electrodes may be reversed. That is, the first electrodes may be bit lines while the second electrodes are word lines.

More specifically, in the organic bistable memory device 7, as shown in Figs. 3 and 4, the first electrodes 3 are arranged on the substrate 2 so that the horizontal direction in the drawing is the longitudinal direction of the first electrodes 3, and the second electrodes 5 are arranged on the substrate 2 so that the vertical direction in the drawing is the longitudinal direction of the second electrodes 5. In the intersecting area of the first electrode and the second electrode, an organic thin film 4 (particularly indicated by a hatch) is stacked between the first electrode and the second electrode (The lower part of the second electrode 5 located in the center of Fig. 3 is not shown).

The organic bistable element according to the present invention is also suitable for use in an organic bistable memory device as shown in Fig. 5. Fig. 5 is a typical cross-sectional view of an organic bistable memory device 10 using the organic bistable element according to the present invention. This organic bistable memory device 10 has a transistor forming area for controlling the organic bistable memory device.

The transistor constituting the transistor forming area may have a conventional construction, and a thin-film transistor (TFT) or MOSFET may be used. In the embodiment shown in the drawing, TFT is used, and the transistor includes a drain electrode 12, a source electrode 13, a gate electrode 14, a gate insulating film 15, and an active layer 16. An extraction electrode 17 is connected to any one (the drain electrode 12 in the drawing) of the drain electrode 12 and the source electrode 13. The extraction electrode 17 is connected to the first electrode 3 in the organic bistable element 1 according to the present invention comprising the first electrode 3, the organic

thin film 4, and the second electrode 5 stacked in that order as viewed from the bottom of the element. An interlayer insulating film 18 is provided on the substrate 2 with the transistor and the like formed thereon except for the extraction electrode 17 part. The organic bistable element 1 according to the present invention is provided on the above-described transistor forming area.

As described above, the organic bistable element according to the present invention is usable, by utilizing its characteristics, for an organic bistable memory device, which can electrically write, read, and erase information, and other applications.

[EXAMPLES]

An organic bistable element having a structure as shown in Fig. 1 was prepared according to the following procedure. At the outset, a clean glass substrate was provided. A 100 nm-thick thin film of aluminum was formed as a lower electrode (a first electrode) on the substrate at a deposition rate of about 0.3 nm/sec by means of a vacuum evaporation apparatus (stock number: VPC-410, manufactured by Shinku Kiko Co., Ltd). In the same manner as described above, a 40 nm-thick first organic thin film of 2-amino-4,5-dicyanoimidazole (manufactured by Tokyo Chemical Industry Co., Ltd.) was formed by the vacuum evaporation apparatus on the thin aluminum film at a deposition rate of about 0.03 nm/sec. A 20 nm-thick thin film of aluminum was deposited on the first organic thin film in the same manner as described above to form an electrically conductive thin film. Further, in the same manner as described above, a 50 nm-thick second organic thin film of 2-amino-4,5-dicyanoimidazole was then formed on the electrically conductive thin film. Finally, in the same manner as described above, a 100 nm-thick thin film of aluminum was formed as an upper electrode (a second electrode) on the second organic thin film. Thus, an organic bistable element 1 was prepared.

Separately, an organic bistable element 2 was prepared in the same manner as in Example 1, except that the thickness of the first organic thin film on the lower electrode side and the thickness of the second organic thin film on the upper electrode side were 40 nm and 70 nm, respectively. Further, an organic bistable element 3 was prepared in the same manner as in Example 1, except that the thickness of the first organic thin film on the lower electrode side and the thickness of the second organic thin film on the upper electrode side were 40 nm and 100 nm, respectively.

An organic bistable element 4 as a comparative bistable element was prepared in the same manner as in Example 1, except that the thickness of the first organic thin film and the thickness of the second organic thin film were 40 nm.

In forming the lower electrode, the organic thin film, and the upper electrode, the degree of vacuum within the chamber of the vacuum evaporation apparatus was kept at about 3×10^{-6} Torr. In the formation of the aluminum film, the target substrate was kept at room temperature, and, in the formation of the organic thin film, the target substrate was kept at 50 to 60°C. Both the thickness of the deposited films and the deposition rate were regulated with a quartz-type film thickness meter (stock number: CRTM 6000, manufactured by ULVAC, Inc.).

Voltage was applied across both the electrodes of the organic bistable element 1 prepared above, and the current flow across both the electrodes was measured with an ammeter (stock number: 237, manufactured by Keithley Instruments, Inc., U.S.A.; this ammeter serves both as a current-voltage meter and a direct-current power source). In the measurement of current-voltage characteristics, in order to prevent the flow of an excessively large current to the element, a limiter on the negative voltage side was set to ± 50 μA. The results of measurement are shown in Figs. 6 and 7. The current values are absolute values of the measured current values.

Voltage was applied, and the potential of the first electrode was decreased from 0 V to conduct negative bias scanning. As a result, as shown in Fig. 6, the current value gradually increased, reached the maximum value at a voltage of about −2 V, and then remained constant as the voltage was decreased to -4 V (as indicated by an arrow 1 in the drawing). This indicates that the organic bistable element was switched (converted) from a high-resistance state (an OFF state) to a low-resistance state (an ON state). When the state of the element before the application of the voltage is presumed to be a state having information of "0," the switching from the high-resistance state (an OFF state) to the low-resistance state indicates that electrical writing of information of "1" was carried out.

Thereafter, scanning was carried out so that the voltage was evenly increased from -4 V to 0 V. As a result, it was found that the measured current value remained at the current value after conversion to the low-resistance state until just before the voltage reached 0 V (as indicated by an arrow 2 in the drawing). This demonstrates that, after switching from the high-resistance state to the low-resistance state, the state of the organic bistable element is stable, that is, the organic bistable element is bistable. The current value in the low-resistance state at an impressed voltage of 1 V was about 10^3 times the current value in the high-resistance state.

Next, scanning was carried out so that the voltage was evenly increased from 0 V. As a result, as shown in Fig. 7, up to about 1.5 V, the current value remained constant (as indicated by an arrow 3 in the drawing). When the voltage was increased to not less than 1.5 V, the absolute value of the current value rapidly decreased (as indicated by an arrow 4 in the drawing). This indicates that the organic bistable element was switched from the low-resistance state (ON state) to the high-resistance state (OFF state). This means that previously written information of "1" was erased and the state was returned to one having information of "0."

Further, in the example of the present invention, it could be confirmed that the element switched to the low-resistance state (ON state) maintained the low-resistance state (ON state) even when the voltage was brought to 0 V. This demonstrates that this organic bistable element is nonvolatile and reading can be carried out without loss of the written information of "1."

The above measurement was also carried out for the organic bistable elements 2 and 3. As a result, it was found that, for both the organic bistable elements 2 and 3, the current/voltage characteristics were similar to those in Example 1. Further, based on these results, a threshold voltage for switching (conversion) from the high-resistance state (OFF state) to the low-resistance state (ON state) and a threshold voltage for resetting from the low-resistance state (ON state) to the high-resistance state (OFF state) were determined, and the relationship between the difference between both the threshold voltages, ΔV, and the difference in thickness between the second organic thin film and the first organic thin film, Δd, was determined. The results were as shown in Fig. 8. The results show that, in a film thickness difference range of 0 nm to 40 nm, the difference between both the threshold voltages increased by about 0.4 V for each 10 nm in film thickness difference.

Next, in driving the organic bistable elements 1 to 3, the current value was limited to 80 μm with an ammeter (stock number: 237, manufactured by Keithley Instruments, Inc., U.S.A.), and voltage was applied to conduct writing of information. Current/voltage characteristics at that time are shown in Fig. 9. Separately, current/voltage characteristics were measured in the same manner as described just above, except that the current value was not limited. The results are shown in Fig. 10. In the experiment wherein no limiter was provided, switching from the high-resistance state (OFF state) to the low-resistance state (ON state) was possible. However, switching from the low-resistance state (ON state) to the high-resistance state (OFF state) was impossible, resulting in malfunction of the element.